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(54) METHOD FOR MAKING A FUEL CELL

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Related U.S. Application Data

- (60) Continuation-in-part of application No. 12/860,210, filed on Aug. 20, 2010, which is a division of application No. 11/228,184, filed on Sep. 16, 2005.
- (51) Int. Cl. H01M 8/00 (2006.01)H01M 8/10 (2006.01)H01M 4/48 (2010.01)
- (52)U.S. Cl.
- Field of Classification Search See application file for complete search history.

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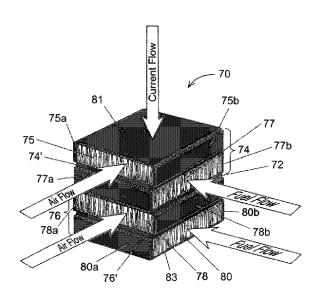
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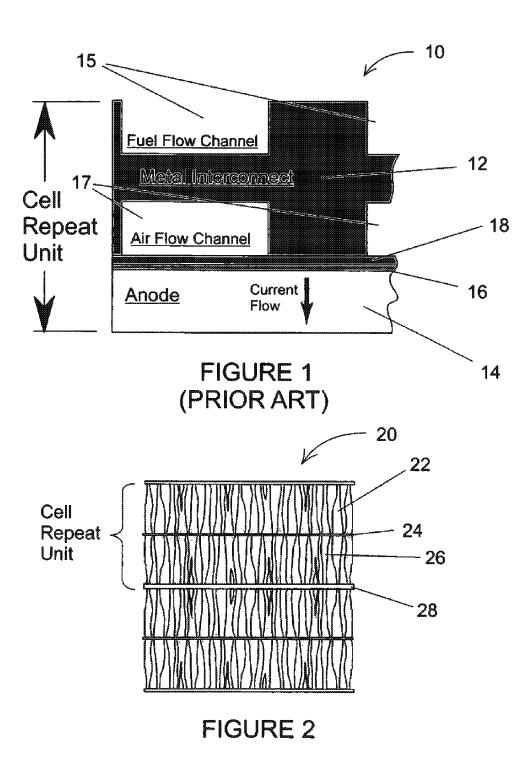
(57)ABSTRACT

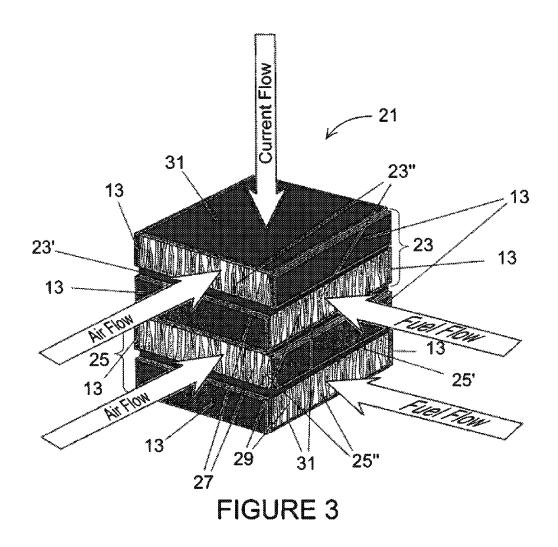
The invention is a novel solid oxide fuel cell (SOFC) stack comprising individual bi-electrode supported fuel cells in which an electrolyte layer is supported between porous electrodes. The porous electrodes may be made from graded pore ceramic tape that has been created by the freeze cast method followed by freeze-drying. Each piece of graded pore tape later becomes a graded pore electrode scaffold that, subsequent to sintering, is made into either an anode or a cathode. The electrode scaffold comprising the anode includes a layer of liquid metal. The pores of the electrode scaffolds gradually increase in diameter as the layer extends away from the electrolyte layer. As a result of this diameter increase, any forces that would tend to pull the liquid metal away from the electrolyte are reduced while maintaining a diffusion path for the fuel. Advantageously, the fuel cell of the invention may utilize a hydrocarbon fuel without pre-processing to remove sulfur.

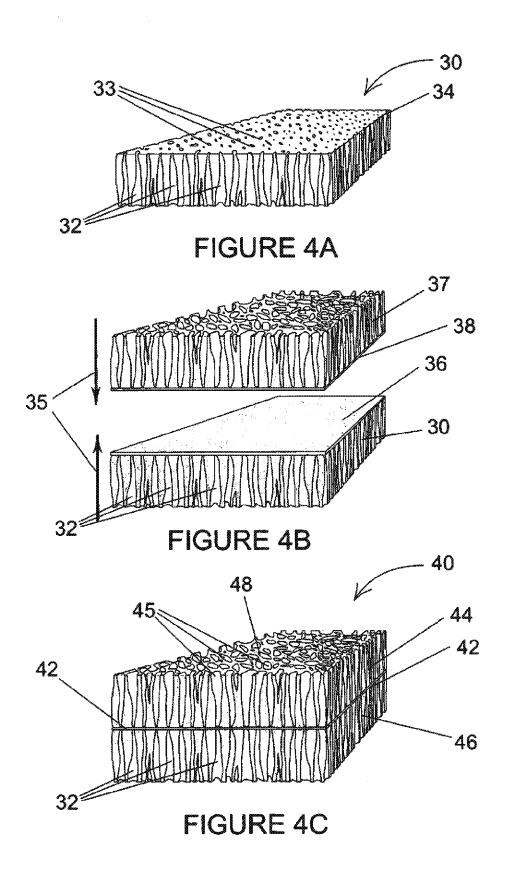
20 Claims, 5 Drawing Sheets



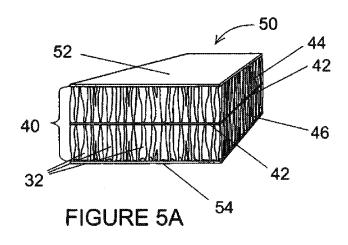
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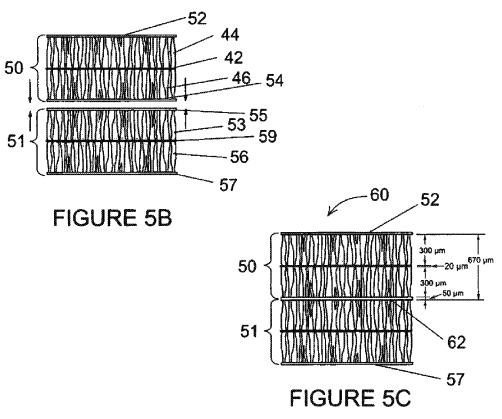






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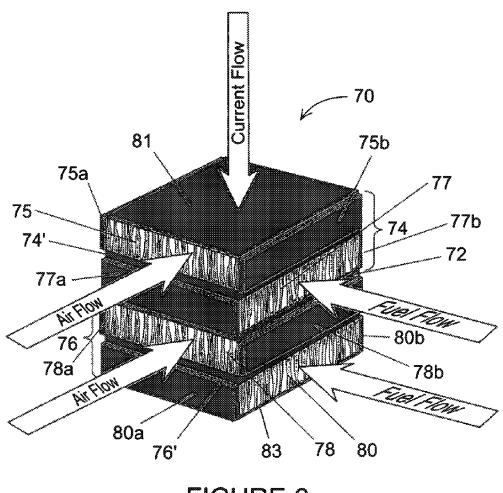


FIGURE 6

METHOD FOR MAKING A FUEL CELL

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority from and is a continuation-in-part application of U.S. Ser. No. 12/860,210, filed on Aug. 20, 2010, entitled "METHOD FOR MAKING A FUEL CELL", which is a divisional of U.S. patent application Ser. No. 11/228,184, filed on Sep. 16, 2005, entitled "MONO-LITHIC SOLID OXIDE FUEL CELL STACK WITH SYM-METRICAL, BI-ELECTRODE SUPPORTED CELLS", which are hereby incorporated by reference in their entirety.

ORIGIN OF THE INVENTION

The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for Government purposes without the payment of any royalties thereon or therefore.

FIELD OF THE INVENTION

The present invention relates generally to fuel cells and fuel cell stacks, and more particularly to high power density 25 solid-oxide fuel cells and the fabrication of unitized stacks of solid oxide fuel cells created from monolithic ceramic frameworks having bi-electrode supporting structure and thin, electrically conductive, non-metallic interconnects between the individual cell repeat units.

BACKGROUND

A majority of solid oxide fuel cell developers are pursuing planar cell geometry with an anode supported cell design 35 (ASC) and metal interconnects. The major challenges of the ASC technology are: cell fabrication and operational reliability; cell electrical contact to the interconnect; and sealing of the cell-to-metal interconnect. The thin electrolyte, normally 10-15 microns thick, is supported on a relatively thick anode 40 made of nickel oxide and yttria stabilized zirconia (NiO—YSZ), which is a cermet having a thickness on the order of 700 to 1,000 microns.

The anode/electrolyte bi-layer is sintered first, followed by application of a thin cathode, usually 25-50 microns thick, 45 which is fired at a lower temperature than the ASC to create a complete, ASC, solid oxide fuel cell (SOFC). Such cells are arrayed in stacks wherein the individual cells are in series electrical contact with one another by means of metal interconnects.

The difficulties in ASC cell and stack fabrication and operation include: 1) shrinkage matching of the thick NiO-YSZ cermet anode and the thin YSZ electrolyte layers during the sintering process; 2) production of flat cell parts for assembly into fuel cell stacks; 3) as the nickel component of 55 the anode cermet is reduced from NiO to Ni metal, the resultant volume change can generate stresses within the anode, sometimes leading to failure of the thin YSZ electrolyte; 4) the anode is sensitive to leaks of oxygen that can cause oxidation of the Ni metal resulting in a sudden expansion of the 60 anode and failure of the cell; 5) provision of sufficient anode thickness to support the electrolyte creates a long pathway for reactant and can lead to diffusion problems in the anode making it hard to achieve high fuel utilization required for high-power commercial applications; 6) ASC cells are fragile 65 and cannot tolerate the high compressive loading that is required for some of the compression type seals used with the

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ASC stacking technology; 7) pore channels of the bulk anode must be relatively narrow in order to give the anode adequate strength, but this limits the rate of gas diffusion into the interior of the thick anode and limits fuel utilization; and 8) the grooved metal interconnects are on the order of 2-3 mm thick and contribute more than 70% of the mass of a stack.

The most critical technical challenges facing all planar SOFC stack developers are the difficulties in providing adequate electrical contact between each cell and its metal interconnect and gas-tight seals. For example, a typical anode supported cell, 7 centimeters in diameter operating at 750° C. has a power density of 0.9 W/cm²; if that same cell is now placed between two metal interconnects, the performance now drops to 0.6 W/cm², a full 33% loss of the power, due simply to electrical contact resistance. Electrical contact resistance, gas sealing, and ease of fabrication are at the center of the new SOFC design.

SUMMARY OF THE INVENTION

A method for making a fuel cell is disclosed. The method includes the step of producing a solid oxide monolith framework. The monolith framework includes a first porous electrode scaffold having a plurality of graded pores, a second porous electrode scaffold having a plurality of graded pores, and a thin electrolyte layer disposed between the first and the second electrode scaffolds. The method further includes the step of impregnating the plurality of graded pores of the first porous electrode scaffold with a liquid metal precursor material. Further, the method includes impregnating the plurality of graded pores of the second porous electrode scaffold with an active cathode material.

A symmetrical bi-electrode supported solid oxide fuel cell is also disclosed. The fuel cell includes a monolith consisting of a sintered oxide material framework including a first porous electrode scaffold having a plurality of graded pores, a second porous electrode scaffold having a plurality of graded pores, and an electrolyte layer that is monolithically disposed between the first electrode scaffold and the second porous electrode scaffold. An anode material comprising a liquid metal precursor material disposed within the plurality of graded pores of the first porous electrode scaffold. In addition, an active cathode material is impregnated within the plurality of graded pores of the second porous electrode.

BRIEF DESCRIPTION OF THE FIGURES

The structure, operation, and advantages of the present invention will become apparent upon consideration of the description herein below taken in conjunction with the accompanying FIGURES. The FIGURES are intended to be illustrative, not limiting. Certain elements in some of the FIGURES may be omitted, or illustrated not-to-scale, for illustrative clarity. The cross-sectional views may be in the form of "slices," or "near-sighted" cross-sectional views, omitting certain background lines that would otherwise be visible in a "true" cross-sectional view, for illustrative clarity.

Although the invention is generally described in the context of these preferred embodiments, it should be understood that the FIGURES are not intended to limit the spirit and scope of the invention to these particular embodiments.

Certain elements in selected ones of the FIGURES may be illustrated not-to-scale, for illustrative clarity. The cross-sectional views, if any, presented herein may be in the form of "slices", or "near-sighted" cross-sectional views, omitting certain background lines which would otherwise be visible in a true cross-sectional view, for illustrative clarity.

Elements of the FIGURES can be numbered such that similar (including identical) elements may be referred to with similar numbers in a single FIGURE. For example, each of a plurality of elements collectively referred to as 199 may be referred to individually as 199a, 199b, 199c, etc. Or, related but modified elements may have the same number but are distinguished by primes. For example, 109, 109', and 109" are three different elements which are similar or related in some way, but have significant modifications, e.g., a tire 109 having a static imbalance versus a different tire 109' of the same design, but having a couple imbalance. Such relationships, if any, between similar elements in the same or different figures will become apparent throughout the specification, including, if applicable, in the claims and abstract.

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The structure, operation, and advantages of the present preferred embodiment of the invention will become further apparent upon consideration of the following description taken in conjunction with the accompanying FIGURES, wherein:

FIG. 1 is an orthogonal schematic side view of a prior art anode supported cell 'repeat unit' with metal interconnects; 20

FIG. 2 is an orthogonal schematic side view of a fuel cell repeat unit, according to the present invention;

FIG. 3 is an oblique schematic view of a monolithic twocell solid oxide fuel cell according to the present invention.

FIG. 4A is an oblique schematic view of a piece of 'green' 25 YSZ tape according to the present invention;

FIG. 4B is an oblique schematic view of two pieces of 'green' YSZ tape, with YSZ electrolyte layers, being brought together;

FIG. 4C is an oblique schematic view of two pieces of 'green' YSZ tape combined into a single complete cell; this view could also be that of a complete sintered cell;

FIG. **5**A is an oblique schematic view of two pieces of 'green' YSZ tape combined into a single complete cell with the interconnect layers printed on each side;

FIG. **5**B is an orthogonal schematic edge view of two cells, ³⁵ with printed on interconnects, being brought together;

FIG. 5C is an orthogonal schematic edge view of two cells, with printed-on interconnects, in a unitized form prior to sintering; and

FIG. **6** is an oblique schematic view of a monolithic two-cell solid oxide fuel cell according to the present invention.

DEFINITIONS

"Aqueous" refers to the liquid component, such as water or 45 organic solvent, of a slurry material.

"Fuel cell" refers to a device comprising an electrolyte that is disposed between two electrodes, one of which reacts with a fuel, the other with an oxidizer.

"Fuel cell stack" refers to a stack of individual fuel cells 50 that are electrically connected to one another in parallel or series to provide electric power at, respectively, low voltage or high voltage.

"Monolith" or "monolithic" refers herein to a unitary ceramic object comprised of sintered solid oxide material.

"Scaffold" a graded pore YSZ tape which, subsequent to sintering, is a porous ceramic that can be treated to impart either anodic or cathodic catalytically active properties.

"Symmetrical" refers to the like thicknesses of the electrodes and the electrode scaffolds that support thin intervening electrolyte layers within each fuel cell repeat unit.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention addresses the difficulties listed hereinabove in the Background section in reference to solid oxide 4

fuel cells based on the anode supported cell (ASC) design. In particular the present invention addresses the problems of differential shrinkage of fuel cell components during high-temperature processing and the weight associated with the massive metal interconnects that are disposed between the individual fuel cells within a fuel cell stack.

The present invention is a novel solid oxide fuel cell (SOFC) stack, and method for making same. The stack according to the present invention comprises individual bielectrode supported fuel cells in which a thin electrolyte layer is supported between porous electrodes of essentially equal thickness. Individual cell repeat units are made from graded pore ceramic 'tape' that has been created by the freeze cast method followed by freeze drying. The plurality of graded pores within each electrode scaffold are introduced by freeze casting of ceramic tape such that each graded pore has a small end and a large end and is oriented more or less perpendicular to major surfaces of the tape and, ultimately, to the thin electrolyte layer. Each piece of graded pore tape later becomes a graded pore electrode scaffold that, subsequent to sintering, is made into either an anode or a cathode by means of appropriate solution and thermal treatment means. Each cell unit is assembled by deposition of a thin coating of ion conducting ceramic material upon the face of each of two pieces of tape surface having the smallest pore openings, and then mating the coated surfaces to create an unsintered electrode scaffold pair sandwiching a thin electrolyte layer. The opposing major outer exposed surfaces of each cell unit is given a thin coating of electrically conductive ceramic, and multiple cell units are stacked, or built up by stacking of individual cell layers, to create an unsintered fuel cell stack. Ceramic or glass edge seals are installed to create flow channels for fuel and air. The cell stack with edge sealants is then sintered into a single monolithic ceramic fuel cell framework. Said solution and thermal treatments means convert the electrode scaffolds into anodes and cathodes. The thin layers of electrically conductive ceramic become the interconnects in the assembled stack. Alternatively, the edge seals can be deposited after the monolithic framework is sintered and then sealed in a second firing.

FIG. 1 is an orthogonal schematic side view of a portion of a prior art single solid oxide fuel cell repeat unit 10. The labeled 'Cell Repeat Unit' 10 is a single fuel cell element comprising, from the top in FIG. 1, a metal interconnect 12, having fuel flow channels 15 (which are adjacent the unshown anode portion of another cell repeat unit), air flow channels 17 adjacent the cathode 18, and electrolyte layer 16.

FIG. 2 is an orthogonal schematic edge view of a fuel cell stack 20 according to the present invention. The comparable fuel cell repeat unit is so labeled, comprising an anode 22 (which can also be referred to in a general way as an 'electrode scaffold' or, more particularly, as an 'anode electrode' or as an 'anode electrode scaffold' or, as explained in detail below, and according to the fabrication process, it could also be a 'cathode electrode' or a 'cathode electrode scaffold'), an electrolyte layer 24, a cathode 26 (which can be referred to in ways comparable to those given parenthetically above in relation to the anode), and an interconnect 28. The thin electrolyte layer 24 has a thickness in the range of about 2 µm to about 200 µm, with a preferred thickness in the range of about 5 μm to about 25 μm. The outermost surfaces of the electrode scaffolds 22, 26 may each have an electrically conductive ceramic coating deposited thereon. The coatings may serve the function of interconnects to other cells in a stack of such sells. The electrode scaffolds 22, 26 may, in an embodiment,

have substantially similar thicknesses, such as in the range of about 100 μm to 1500 μm with a most desired range of about 300 μm to about 750 μm .

Each bi-electrode supported fuel cell repeat unit of the two-cell stack 20 in FIG. 2, and all structural and supporting parts of the fuel cell stack according to the present invention, is, upon completion of the stack fabrication process, a single sintered solid oxide monolith which, subsequent to the high-temperature sintering process that results in a cell stack monolith, is subsequently subjected to solution and thermal treatment means wherein the electrode scaffolds 22, 26 acquire their respective anodic and cathodic catalytic properties. Said solution and thermal treatment means are described in more detail herein below but, briefly, entail treatments with aqueous solutions of metal salts or suspensions of oxides and with heat so as to impart to the electrode scaffolds 22, 26 the catalytically active properties of anodes and cathodes.

FIG. 3 is an oblique schematic view of a complete monolithic solid oxide fuel cell 21 according to the present invention. FIG. 3 can as well be said to represent a 'green' fuel cell 20 framework 21, i.e., prior to sintering, or a sintered ceramic framework immediately after sintering and before the electrode scaffolds (22,26 in FIG. 2) have been subjected to solution and thermal treatment means, described herein below, to impart to them anodic and cathodic catalytic activi- 25 ties. Shown also in FIG. 3 are repeat cell units 23, 25 and their respective thin electrolyte layers 23', 25' which are disposed between first and second respective porous electrode scaffolds 23", 25", which could as well be referred to as actual electrodes, depending upon the stage of completion (sintered 30 or not, with or without solution and thermal treatments means applied to the electrode scaffolds) of the assembly 21. The electrode scaffolds 23", 25" comprise a plurality of graded pores that may be oriented more or less perpendicular to the electrolyte layer 23', 25'. The pores are graded in size such 35 that the smallest ends of the pores are adjacent to the electrolyte layer 23', 25', and the largest ends of the pores are disposed most distal from the electrolyte layers 23', 25'. For example, the graded pores of the electrode scaffolds 23", 25" may have characteristic small diametrical pore dimensions of 40 between 0.5 μm and 15 μm, and most preferably of between 2 μm and 10 μm, and the characteristic large pore dimensions between 25 µm and 125 µm, and most preferably between 50 μm and 100 μm.

Interconnects **31** are shown on the top and bottom of the 45 stack **21**, with one being disposed between the individual cells **23**, **25**. The interconnects **31** are made of thin layers of electrically conductive ceramic or of cermet. The interconnects **31** each has a thickness in the range of about 2 μ m to about 200 μ m, with a preferred thickness in the range of about 50 μ m to about 25 μ m. Nonconductive edge sealants **13**, which are made of a nonconductive material selected from the group consisting essentially of ceramic or glass, direct the flow of air and fuel respectively through porous electrode faces **27** and **29**. All components shown in FIG. **3** are made of materials 55 having at least the shared property of having essentially the same coefficient of thermal expansion.

Referring again to FIG. 2, it should be noted that the fuel cell stack subassembly 20 may be made essentially of one material that is selected from a class of materials consisting 60 essentially of ionic conductors. More generally, the one material may be selected from a general class of solid ceramic materials comprising ionic conductors of either protons, or, preferably in relation to embodiments of this invention, oxygen ions. In an embodiment, the fuel stack subassembly may 65 be made mostly of a single ceramic material, such as yttria stabilized zirconia (YSZ), or other material selected from the

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class of materials that includes ionic conductors, either protons or oxygen ions and preferably oxygen ions. In the case of protonic conductors, the main material of the subassembly 20 may be made of the general class of materials such as doped barium cerate (BaCeO₃) or doped strontium cerate (SrCeO₃), doped barium zirconate (BaZrO₃) or strontium zirconate (SrZrO₃) and mixtures of these, and not limited to these materials, as long as the materials are stable in both the reducing and oxidizing environments to which the cell is exposed. In the case of oxygen ion conductors, many of which have the fluorite crystal structure, the subassembly 20 is made of the general class of materials such as doped zirconia (ZrO₂), doped ceria (CeO₂) and other doped oxides of metals such as bismuth, hafnium, thorium, indium or uranium. More specifically, oxide ion conductors include materials such as yttria stabilized zirconia (YSZ or 8YSZ), partially stabilized zirconia such as 3YSZ, scandia stabilized zirconia (ScSZ), gadolinium doped ceria (GDC) or other commonly doped cerias such as samarium or yttrium (SDC or YDC), and a perovskite oxide conductor, strontium and magnesium-doped lanthanum gallate or LSGM (LaSrGaMgO₃). In an embodiment, the interconnect 28 is an electrically conductive ceramic, such as doped lanthanum chromite (LaCrO₃). Doped lanthanum chromite is a perovskite with the ABO₃ structure and it can be doped at either the A-site or B-site or both, to improve the sinterability, shrinkage match, thermal expansion match, conductivity, etc. of the interconnect to the remainder of the fuel cell system. Suitable dopants might include Mg, Ca, Sr, Co, Y, Ni, Ti, Cu, Mn, V, Pr, Al, and mixtures of these and are not limited to these. The doped LaCrO₃ powder might also be produced either A-site rich or A-site deficient where the A/B site ratio is not equal to 1.0.

Referring now to FIGS. 4A through 4C, selected parts of the fabrication sequence for a single cell are recapitulated from U.S. Pat. No. 7,534,519, assigned to the assignee of the present invention, entitled, SYMMETRICAL BI-ELEC-TRODE SUPPORTED CELL FOR SOLID OXIDE FUEL CELLS, which is incorporated in its entirety herein by reference hereto, so as to explain the complete fabrication process of a solid oxide fuel cell stack according to present invention. The freeze-tape casting technology may produce the aforementioned graded pore size in the respective electrode portions. As a brief summary of an embodiment, the freeze-tape casting method may begin with traditional tape casting methods wherein an aqueous ceramic slip material is cast onto a carrier film made of thermosetting plastic or thermoplastic or other suitable film material by means of a doctor blade apparatus. Directional freezing of the tape (or slip), which causes the formation of graded pores is followed by freeze drying to produce unsintered or "green" tape, having the desired graded porosity in which the side of the tape that is in contact with the film has smaller pores than those on the other side. A polymer may be incorporated into the slip as to impart flexibility to the resultant cast tape after it is freeze dried. If the aqueous carrier solvent is water, for example, a polymer such as acrylic latex emulsions or more traditional polyvinyl alcohol (PVA) or other methocel are used. If the carrier solvent is organic (such as terpineol and/or tertiary butyl alcohol), then the polymer may be polyvinyl butyral or ethyl cellulose. Freezing of the tape is such as to cause the directional growth of the solvent crystals to form pores whose characteristic interstitial dimensions increase in rough proportion to the distance from the underlying film. The freeze-tape casting process has been developed as a method of forming and controlling complex pore structures without having to use thermally fugitive pore formers. It is ideally suited for fabrication of a symmetrically bi-electrode supported fuel cell wherein the resultant graded

pores can be tailored in size and other structural characteristics for fuel and air diffusion within the two respective electrode scaffolds that ultimately become catalytically active electrodes, namely an anode and a cathode. Freeze casting provides a high degree of open porosity that is not easily 5 achieved with traditional pore forming technologies.

FIG. 4A illustrates in oblique schematic view a rectangular section of 'green tape' 30 (i.e., freeze dried but unsintered) that is characterized by aligned graded pores 32, the graded porosity of which derives from the tape freeze casting process or method taught in the aforesaid patent in reference to the creation of a single monolithic fuel cell framework. The graded-pore green tape 30 may be flexible by virtue of including a polymer such as methocel if the solvent is water, or, if an organic solvent is used, other polymers, such as polyvinyl 15 butyral (PVB). The tape segment 30 has a thickness (t) of the green tape in the range of 100 µm to 1,500 µm and a preferred range of 300 μm to 750 μm. The characteristic width dimensions of the graded pores 32 are such that the smallest pore openings 33 are on one face 34. The characterizing dimen- 20 sions of the graded pores 32 are such that the characteristic small pore dimension is between 0.2 um and 15 µm, with a preferred range of between 0.5 µm and 10 µm, and the characteristic large pore dimensions is between 25 µm and 125 μm, and most preferably of between 50 μm and 100 μm. The 25 green tape 30 is made of such materials as yttria stabilized zirconia (YSZ), or the general class of materials comprising ionic conductors, either protonic or oxygen ionic and preferable oxygen ionic. In the case of a protonic conductors the monolith 20 is made of the general class of materials such as 30 doped barium cerate (BaCeO₃) or doped strontium cerate (SrCeO₃), doped barium zirconate (BaZrO₃) or strontium zirconate (SrZrO3) and mixtures of these, and not limited to these materials, as long as the materials are stable in both the reducing and oxidizing environments to which the cell is 35 exposed. In the case of oxygen ion conductors, many of which have the fluorite crystal structure, materials such as doped zirconia (ZrO₂), doped ceria (CeO₂) and other doped oxides of metals such as bismuth, hafnium, thorium, indium or uranium. More specifically, oxide ion conductors of materials 40 such as yttria stabilized zirconia (YSZ or 8YSZ), partially stabilized zirconia such as 3YSZ, scandia stabilized zirconia (ScSZ), gadolinium doped ceria (GDC) or other commonly doped cerias such as samarium or yttrium (SDC or YDC), and a perovskite oxide conductor, strontium and magnesium- 45 doped lanthanum gallate or LSGM (LaSrGaMgO₃) along with the aforementioned admixture of a suitable polymeric material which is burned off during the subsequent hightemperature sintering process that serves to fuse the structural components of the fuel cell stack 21 (FIG. 3) into a single 50 ceramic monolithic fuel cell stack, or stack framework if the electrode scaffolds 23", 25" have not yet been subjected to the treatment means that imparts the required anodic and cathodic catalytic activity.

In the remaining portion of this description, YSZ is used to 55 refer generally, generically and specifically to be the material from which the main structural elements, i.e., electrode scaffolds and electrolyte layers, of the fuel cell stack are made. However, this reference should not be deemed as limiting the type of material used.

FIG. 4B shows in oblique schematic view the green tape 30 of FIG. 4A, with its surface 34 (in FIG. 4A) coated with a thin and nonporous layer of YSZ 'ink' 36. In an embodiment, the thickness of the layer of YSZ 'ink' 36 may be substantially less than the thickness of the green tape 30, such as about 10 65 micrometers. Shown in FIG. 4B above the ink coated tape 30 is a second piece of tape 37 that also has a thin and nonporous

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ink layer 38, oriented such that the two inked layers 36, 38 are facing one another prior to being brought together as indicated by the arrows 35, the result being that the two inked layers, which might or might not have dried completely after being applied, merge into a single nonporous electrolyte layer 42, as shown in FIG. 4C. The same structure may be obtained by substituting green YSZ electrolyte tape for the layer of YSZ ink.

FIG. 4C is an oblique schematic view of a single YSZ layered structure, or cell framework, 40 comprising a first electrode scaffold 44 and a second electrode scaffold 46, with the intervening electrolyte layer 42 disposed there between. This layered single-cell framework structure 40 can, upon completion of high temperature sintering during which the polymeric components of the YSZ is burned away, become one operative fuel cell part of single monolithic framework for a solid oxide fuel cell as described in the aforementioned patent entitled, SYMMETRICAL BI-ELECTRODE SUP-PORTED CELL FOR SOLID OXIDE FUEL CELLS. Note that the graded porosities 32 of the two electrode scaffolds 44. 46 are oriented such that the larger pore openings 45 are visible on the upper surface 48 of the electrode scaffold 44; in other words, the small ends of each of the graded porosities 32 are adjacent the thin electrolyte layer 42, while the large ends 45 (visible on the top surface 48 only in FIG. 4C) are distal from the electrolyte layer.

Fabrication of a Fuel Cell Stack

The cell 40 of FIG. 4C is exemplary of a single fuel cell that when stacked with like cells results in a multi-celled fuel cell stack 20 of the sort shown schematically in FIG. 2. Those skilled in these particular arts will recognize that the sequence of making a stack consisting of a plurality of individual fuel cells could proceed in such a way that individuals cells 40 could be stacked as described below, or the individual layers of graded pore YSZ tape and nonporous electrolyte layers 42 could be individually treated and stacked one upon another prior to sintering. The cell-stacking procedure that is described herein below assumes that individual cells 40 are treated as follows and then stacked one upon another.

FIG. 5A shows an individual cell framework 50 which contains the cell 40 shown in FIG. 4C, but with additional nonporous coatings 52, 54, top and bottom, covering the large pore holes 45 shown in FIG. 3C. Said coatings 52, 54 are sprayed, printed, or deposited uniformly by other similar means as a liquid slurry or as green tape upon the large pore surfaces (which are not visible in FIG. 5A), and then allowed to dry. The thin, nonporous layers 52, 54 are made of an electrically conductive ceramic, such as doped lanthanum chromite (LaCrO₃), and may be doped to improve the sinterability, shrinkage match, thermal expansion match, conductivity, etc. of the interconnect, to the remainder of the fuel cell system. Suitable dopants might include Mg, Ca, Sr, Co, Y, Ni, Ti, Cu, Mn, V, Pr or others as will be appreciated by those having ordinary skill in the art. Doped LaCrO₃ has a coefficient of thermal expansion that is sufficiently similar to that of the electrode scaffolds 44, 46 and the electrolyte layers 42 so that the high temperatures of the sintering and subsequent heating processing, including operation of the completed fuel cell, does not give rise to stresses that might lead to failure 60 during fabrication or unreliability of service of the finished fuel cell stack. The liquid slurry, organic based, form in which the layers 52, 54 are deposited, also contain a polymer component such as polyvinyl butyral (PVB), that is removable by burning that may occur during the sintering of the assembled fuel cell stack.

The polymeric compounds that are included in the various 'green' (i.e., unsintered) layers of YSZ (electrodes scaffold

and the electrolyte layers) and doped LaCrO₃ interconnect layers, such as **52**, **54** in FIG. **5A**, impart a degree of flexibility to the various cell layers, thereby aiding in the intimate mating of the cell component layers with one another prior to sintering. The layered structure **50** is essentially a green (i.e., 5 unsintered) fuel cell repeat unit.

FIG. 5B is an orthogonal edge schematic view of two cells 50,51 being brought together, cell 50 being the one shown in FIG. 5A, and cell 51 being of the same sort, comprising two layers of doped LaCrO₃ 55,57, two electrode scaffolds 53,56, 10 and an electrolyte layer 59.

FIG. 5C as an orthogonal edge view of a two-cell stack or metastructure 60, comprising the cells 50 and 51 of FIG. 5B. That is, the two (or more) layered structures 50, 51 are mated into a single metastructure 60. Note that the two layers 54, 55 shown in FIG. 5B are shown as a single interconnect layer 62 in FIG. 5C. In other words, the stacking of the cells 50, 51 can be done while the layers 54, 55 of FIG. 5B are not fully dried, or, even if they are fully dried, they will become unified into the single contiguous interconnect layer 62 during the final sintering process. Those who are skilled in the art should easily recognize that additional cells can be added to the stack 60 prior to sintering and that a single green tape can be used to produce the interconnect in place of ink.

In an embodiment, there may be basically three types of 25 materials in the stack 21 (FIG. 3) that go into the sintering furnace, namely the YSZ components (electrode scaffolds and electrolyte layers), the doped LaCrO₃ interconnect layers, and the edge sealants 13 (FIG. 3), all of which have essentially the same thermal expansion coefficients and can 30 be tailored so as to be sintered at the same time, rate, and temperature.

Prior to final sintering, the dense and non-porous edge seals 13 (FIG. 3) must be put in place so as to direct the cross flow of air and fuel as shown also in FIG. 6, which is an oblique 35 schematic view of a two-cell stack 70 having a single interconnect 72 between the two cells 74,76. The cells 74, 76, including electrolyte layers 74', 76' respectively, have attached to them opposing sets of edge seals 75a, 75b, 77a, 77b, 78a, 78b, 80a, 80b. In an embodiment, the edges seals 40 **75***a*, **75***b*, **77***a*, **77***b*, **78***a*, **78***b*, **80***a*, **80***b* are applied as an aqueous paste of YSZ or other materials listed elsewhere herein above having coefficients of thermal expansion essentially the same as that of the other components of the monolithic solid oxide fuel cell stack 70. The edge seals 75a, 75b 45 and 78a, 78b serve the function of creating flow channels for air moving into and through the two respective porous cathode electrodes faces 75, 78, and the seals 77a, 77b and 80a, 80b create flow channels for fuel through the two anode electrode faces 77 and 80. Alternatively the edge seals can be 50 added after the first sintering procedure and bonded in a second sintering step.

As should be apparent to those skilled in the art, FIG. **6** is a two-cell exemplary representation of a multi-cell fuel cell stack. The interconnects **81** and **83** at the top and bottom of the 55 stack **70** communicate electrical current flow to and from external electrical loads. The edge seals **75***a*, **75***b*, **77***a*, **77***b*, **78***a*, **78***b*, **80***a*, **80***b* might, under certain conditions, be made of a glass ceramic rather than from YSZ, and they may contain a polymeric compound when the sealant material is applied to 60 the stack **70** prior to sintering.

After a multi-cell stack **70** of FIG. **6** is assembled, including its edge seals, it is allowed to dry thoroughly and then put into a sintering furnace for sufficient time of 10 minutes to 10 hours, preferably 1-2 hours, and at sufficient temperature of 65 typically 1400 to 1700° C., ideally 1350-1400° C. to cause the particles to fuse, such as the solid oxide particles of YSZ to at

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least partially fuse to LaCrO₃. Because the cells and cell stack, in the green unsintered state, are all ceramic, except for the polymer components, sintering temperatures can be optimized for densification of the electrolyte, scaffold and interconnect layers without concerns of reactions of YSZ with the electrode materials, which are added later. The sintered result is a single monolithic fuel cell stack framework that, upon treatment subsequent to sintering, converts the porous electrode scaffolds into the necessary anode and cathode electrodes, the result being an operational fuel cell stack that, when fed fuel and air, can produce an electric current.

In the final steps of fabrication, subsequent to sintering, the electrode scaffolds are subjected to solution and thermal treatment means wherein a suitable solution of metal salts or suspension of metal oxides is pulled by capillary action into one set of electrode scaffolds and a different solution of metal salts or oxides is pulled by capillary action into the other set of electrode scaffolds. Subsequent heating of the solution treated scaffolds converts the metal salts or oxides into catalytically active forms that impart anodic properties to one set of electrode scaffolds and cathodic properties to the other set of scaffolds and bonds them to the scaffold, electrolyte, and interconnect surfaces. The means also includes that the cathodic scaffolds of the stack must be masked off so that only the porous fuel channels in the electrode scaffolds can be exposed and active anode materials, such as Ni metal [Co, Cu, Fe, Pt, Pd], are infiltrated, as salt, nitrate, carbonate, chloride, oxide or other solutions, into the porous anode region; the nickel compound later becomes an active metallic, electrocatalyst. The anode channels are then masked and the air channels are infiltrated with active cathode materials, such as lanthum ferrite (LaFeO₃) or lanthanum manganite (LaMnO₃), which are p-type perovskites that typically are doped with rare earth elements (e.g., Sr, Ce, Pr, Ca, Co, Fe, Cu, Ga, etc. but not limited to these) to enhance their conductivity. Most often they are doped with strontium and referred to as LSF (La_{1-x}Sr_xFeO₃) or LSM (La_{1-x}Sr_xMnO₃). Other potential cathode materials include indium oxide, commonly doped with oxides of Sn, Pr or Zr.

In another embodiment, subsequent to sintering and cooling of the monolithic framework, such as framework 50, the electrode scaffolds 44,53 (shown in FIG. 5B), may be imparted with anododic properties by use of a liquid metal chemical precursor. An example of such a liquid is Tin-isopropoxide, which then decomposes and is eventually reduced to the metal state for the desired liquid Sn. Specifically, the electrode scaffolds 44.53 may involve the capillary uptake of the liquid metal precursor. The liquid metal precursor may be imparted by blocking the scaffold of the other electrode, such as the scaffold of the electrode 46,56 that will have cathodic properties. For example, each end of the flow channels of the electrode scaffold (not receiving the liquid metal precursor) is masked off to plug the flow channels with a suitable polymer, such as polypropylene carbonate dissolved in acetone, while the other electrode is infiltrated with the liquid metal precursor. Non-limiting examples of the liquid metal precursor that may be used include but should not be deemed as limited to tin (Sn), gallium (Ga), indium (In), antimony (Sb), thallium (Ti), lead (Pb), bismuth (Bi), silver (Ag), gold (Au), copper (Cu), polonium (Po), platinum (Pt), palladium (Pd) and bimetallic mixtures and/or other metallic forming chemical mixtures. Advantageously, the liquid metal may be positioned and maintained near the electrolyte 42 by the natural gradient of porosity and capillary forces of the pores of the electrode scaffolds. As a result, only a relatively small amount of liquid metal may be required, such as only 20 to 50 microns. In this embodiment the liquid Sn is not held in a reservoir. Reactant

gases pass over the liquid Sn layer, not through it. By producing just a thin liquid Sn layer, the surface area for chemical reaction is greatly increased.

The symmetrical bi-electrode supported fuel cell ("BSC") design described herein is advantageous in the use of liquid 5 metal as it permits an electrolyte having a significantly lower thickness than tubular designs. For example, tubular designs may have electrolytes that are at least 300-400 microns thick and have supports that are over 1500 microns thick. The thick porous support of these tubular designs can cause diffusion 10 problems and coking with the fuel. In addition, the thick electrolyte results in high resistance and reduces the power density. As a result, the BSC design described herein provides significant advantages for the use with a liquid metal electrode. Advantageously, embodiments of the present invention 15 permit electrolyte thicknesses that may be, for example, on the order of 30 microns.

As described above, the pores of the electrode scaffolds gradually increase in diameter as the layer extends away from the electrolyte layer 42, 59. As a result of this diameter 20 increase, any forces that would tend to pull the liquid metal away from the electrolyte 42,59 are reduced while maintaining a diffusion path for the fuel. Accordingly, coking or other diffusion issues are avoided due to the pore design. Use of liquid metal also may permit use of a liquid fuel, such as a 25 hydrocarbon fuel. Examples of hydrocarbon fuels that may be used with the invention include but are by no means limited to JP-8, natural gas, gasoline, diesel fuel, methanol, and/or coal gas. An exceptional benefit of this embodiment is that the fuel cell may be operated without pre-processing of the hydrocarbon fuel. For example, JP-8 fuel may be used directly without prior removal of the sulfur and results in the production of electricity.

In operation, the hydrocarbon fuel operates directly on the hydrocarbon fuels. As the oxygen ions move through the 35 electrolyte 42,59, the oxygen ions react with the liquid metal to form a metal oxide. In an embodiment where the liquid metal is tin, the oxygen ions react to form tin oxide (SnO_2) . The metal oxide then reacts (or oxidizes) with the hydrocarbon fuel, losing the oxygen and rereducing the metal oxide to 40 its metallic state.

The inventors have tested liquid infiltration into the electrode scaffolds and have found that the solutions travel over distances of centimeters very quickly, even without a vacuum, due to the strong capillary action of the graded pores of the 45 electrolyte scaffolds.

By using the YSZ electrode scaffolds as turbulent diffusion channels for fuel and air, with a thin interconnect on the order of 50 microns, the power density (kw/kg) and simplicity of the BSC stack is increased.

In summary, the BSC fuel cell stack according to the present invention provides a number of advantages when compared to other planar fuel cell designs. The freeze-tape casting technology, which allows for graded porosity to be incorporated into the green tape in a single step, greatly 55 simplifies the fabrication of the BSC cells and adds processing flexibility which can be used to optimize the BSC cells and stacks for optimum performance. Some of the advantages of the BSC stack design are: 1) the thin electrolyte and porous support may be made of a single material, such as YSZ, 60 making fabrication and sintering less challenging; 2) the porous electrode scaffolds of each cell protect each thin electrolyte layer from the stresses created by the conventional Ni metal anode which has a higher coefficient of thermal expansion; 3) the porous supports may be infiltrated at the outer 65 edges, with YSZ or other ceramic or glass materials with matched coefficients of thermal expansion ("CTE"), to pro12

vide for hermetic seals that are fully dense upon completion of sintering; 4) each ceramic interconnect is supported so that a thin, dense layer of doped material, such as LaCrO₃, may be applied to reduce the electrical resistance of the non-metallic interconnect; 5) gas channels are provided by the graded porosity in the support, which allows the ceramic interconnect to be flat, without channels or grooves, making fabrication and sintering less complex which essentially decreases the cost/weight while increasing the power density; 6) both interfaces at the electrolyte/electrode support and interconnect/electrode support are rough with a large amount of surface area to provide intimate contact with the active electrode materials which reduces interfacial resistance; 7) coating the exposed surfaces of the porous support structures with active electrode materials, after sintering, provides intimate electrical contact between the cell and the interconnect, a major problem of other designs, reducing the internal stack resistance; 8) an anode with graded porosity will be less susceptible to diffusion limitations and should achieve high fuel utilization which is a problem with traditional anode supported cells with a uniform pore structure; 9) a wider selection of cathode and anode materials, some with CTEs higher than YSZ, can be used since the materials will not be exposed to the high temperature of the first sintering step of the stacked YSZ electrode scaffolds, electrolyte and interconnects; 10) because of the symmetrical cell design which reduces stresses, alternative electrolyte materials with higher ionic conductivity, such as LaSrGaMgO₃ can be used; 11) the stack can be operated at higher temperatures since it uses more traditional ceramic interconnect materials, with proven long life and stability, rather than metal interconnects; and 12) the YSZ support structure in the cell makes both the electrodes and the seals more tolerant of thermal cycles and oxidationreduction cycles.

By using thin ceramic interconnects as the separator plates for hydrogen and fuel, in conjunction with the porous YSZ scaffolds for gas diffusion, the BSC stack essentially removes the weight and volume of the thick metal interconnect used in stacks of anode-supported cells. Estimates for the specific power density of an ASC stack, producing 0.4 W/cm² of active electrode area, are on the order of 1.3 kW/L and 0.28 kW/kg. By comparison, taking into account only the active cell area, a BSC stack generating the same 0.4 W/cm² would have a specific power density of 6.0 kW/L and 1.37 kW/kg.

A Second Embodiment

The inventors envision a second embodiment of their solid oxide fuel cell stack invention wherein the invention is modified as described below for the purpose of providing crew life support for NASA exploration missions including surface habitat and EVA suit implementation. More specifically, the present invention can be modified and optimized to perform electrolysis on the $\rm CO_2$ so as to produce breathable oxygen in $\rm CO_2$ rich settings, such as the surface of Mars.

Modification and optimization of the present invention would include the use of electrocatalysts tailored for electrolysis of CO₂. The advantages would include low weight, durability, and high efficiency and specific power density.

The atmosphere on Mars, for example, is 95% CO₂, making it an obvious source of O₂. A single solid oxide fuel cell has successfully demonstrated the production of O₂ from the electrolysis of CO₂. The products of the electrolysis are pure O₂ and CO and the power required to produce the O₂ may

come from solar power. Also, said fuel cell would also be reversible and able to generate power from the stored CO and O_2 are used as fuel.

A Third Embodiment

The inventors envision a third embodiment of their solid oxide fuel cell stack invention wherein the invention is modified as described below for the purpose of providing crew life support for NASA exploration missions including surface 10 habitat and EVA suit implementation. More specifically, the present invention can be modified and optimized to perform electrolysis on the $\rm H_2O$ present in the astronaut suits so as to produce breathable oxygen. Said fuel cells is also reversible and able to generate power from the stored $\rm H_2$ and $\rm O_2$ are used 15 as fuel.

Modification and optimization of the present invention would include the use of electrocatalysts tailored for electrolysis of $\rm H_2O$ or $\rm CO_2$. The advantages would include low weight, durability, and high efficiency and specific power 20 density.

Heretofore, only fuel cells having very thick YSZ electrolytes, on the order of 300 to 600 microns thick, have been demonstrated (see AIAA 2000-1068 "Update on the Oxygen Generator System for the 2001 Mars Surveyor Mission," Sridhar, et. al). The thick electrolytes result in very high cell resistance to ionic flow and therefore are characterized by a low rate of oxygen production. Such prior art cells also use platinum or silver electrodes that are not ideal for this application and add significant cost to development and manufac- 30 ture. Additionally, and as pointed out hereinabove in relation to prior art solid oxide fuel cells, the previous fuel cell stack designs use heavy metallic interconnect plates between the cells, which significantly increase the stack volume and weight. Said metal interconnects are prone to corrosion and 35 have historically been very difficult to seal against the YSZ ceramic cell. This is of considerable importance for O_2 separation where nearly hermetic seals, capable of withstanding frequent thermal cycles, are required.

Adaptation of the fuel cell or fuel cell stack according to the present invention would require that the electrode scaffolds would be infiltrated with suitable materials, by solution and thermal treatment means similar to those described hereinabove, to provide catalytically active CO₂ and O₂ electrodes. A specific improvement for this embodiment would be electrode compositions that are more active for CO₂ reduction or CO oxidation. Initial studies found that platinum electrodes encountered some degradation due to strong CO adsorption during operation in fuel cell mode. A more active electrode for the CO/CO₂ side of the cell would be Cu or Cu—Ce-based materials since copper is a good oxidation catalyst. A more active electrode for the O₂ side of the cell would be mixed conductive perovskite materials, including doped LaFeO₃, doped LaCoO₃ and doped LaNiO₃ or mixtures of these materials

While the main interest for electrolysis of CO_2 to produce O_2 comes from NASA for a manned mission to Mars, in a broader sense, reversible fuel cells have many applications for other space missions, such as lunar bases and space stations, where they provide both O_2 and power. SOFC technology can be used in all these applications, regardless of whether the requirement is for CO_2 electrolysis or $\mathrm{H}_2\mathrm{O}$ electrolysis. The BSC according to the present invention offers advantages in each case, since it provides for a very thin electrolyte which is balanced on both sides, making it easier to manufacture and more durable. It also allows for more freedom to choose a wider composition of electrodes, making

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it easier to optimize the electrodes to fit the application. All of these same benefits are applicable to commercial SOFC markets, regardless of whether they are for aerospace, automotive or stationary applications.

Although the invention has been shown and described with respect to a certain preferred embodiment or embodiments, certain equivalent alterations and modifications will occur to others skilled in the art upon the reading and understanding of this specification and the annexed drawings. In particular regard to the various functions performed by the above described components (assemblies, devices, circuits, etc.) the terms (including a reference to a "means") used to describe such components are intended to correspond, unless otherwise indicated, to any component which performs the specified function of the described component (i.e., that is functionally equivalent), even though not structurally equivalent to the disclosed structure which performs the function in the herein illustrated exemplary embodiments of the invention. In addition, while a particular feature of the invention may have been disclosed with respect to only one of several embodiments, such feature may be combined with one or more features of the other embodiments as may be desired and advantageous for any given or particular application.

The invention claimed is:

- A method for making a fuel cell comprising: producing a solid oxide, non-electrically conductive, unitary ceramic monolith framework including:
 - a first porous electrode scaffold having a plurality of graded pores and no active anode material;
 - a second porous electrode scaffold having a plurality of graded pores and no active cathode material; and
 - a thin electrolyte layer disposed between the first and the second electrode scaffolds; and
- impregnating the plurality of graded pores of the first porous electrode scaffold with an electrically conductive liquid metal material and impregnating the plurality of graded pores of the second porous electrode scaffold with an electrically conductive active cathode material.
- equent thermal cycles, are required.

 Adaptation of the fuel cell or fuel cell stack according to the esent invention would require that the electrode scaffolds antimony, thallium, lead, bismuth, silver, gold, copper, polonymum, and the infiltrated with suitable materials, by solution and prime the state of the stat
 - 3. The method of claim 1 wherein the step of impregnating the plurality of graded pores of the first porous electrode scaffold with a liquid metal material include masking or plugging flow channels of the second porous electrode with a polymer.
 - 4. The method of claim 3 wherein the polymer is polypropylene carbonate dissolved in acetone.
 - 5. The method of claim 1 wherein the plurality of graded pores of the first porous electrode gradually have a first diameter at a first distance from the electrolyte layer and a second diameter at a second distance from the electrolyte layer, and further wherein the second diameter is greater than the first distance.
 - **6**. The method of claim **1** wherein the liquid metal reacts with hydrocarbon fuel and the second porous electrode reacts with oxygen to produce electrical current.
 - 7. The method of claim ${\bf 1}$ wherein the hydrocarbon is used as fuel without prior removal of sulfur.
 - 8. The method of claim 6 wherein oxygen ions react with the liquid metal to form a metal oxide.
 - **9**. The method of claim **8** wherein the metal reacts with the hydrocarbon fuel to reduce the metal oxide to a metallic state.
 - 10. The method of claim 1 wherein the plurality of graded pores of the first porous electrode and the second porous

electrode extend substantially perpendicular to the electrolyte layer, and further therein a diameter of the plurality of graded pores gradually increases in size as the first porous electrode and the second porous electrode extends away from the electrolyte layer.

- 11. A symmetrical bi-electrode supported solid oxide fuel cell comprising:
 - a monolith consisting of a sintered oxide, non-electrically conductive, unitary ceramic material framework including:
 - a first porous electrode scaffold having a plurality of graded pores and no active anode material;
 - a second porous electrode scaffold having a plurality of graded pores and no active cathode material; and
 - an electrolyte layer that is monolithically disposed 15 between the first electrode scaffold and the second porous electrode scaffold;
 - an anode material comprising at least an electrically conductive liquid metal is impregnated within the plurality of graded pores of the first porous electrode scaffold, and 20 an electrically conductive active cathode material is impregnated within the plurality of graded pores of the second porous electrode.
- 12. The symmetrical bi-electrode supported solid oxide fuel cell of claim 11 wherein the liquid metal is selected from 25 the group consisting of: tin, gallium, indium, antimony, thallium, lead, bismuth, silver, gold, copper, polonium.
- 13. The symmetrical bi-electrode supported solid oxide fuel cell of claim 11 wherein the plurality of graded pores of the first porous electrode gradually have a first diameter at a 30 first distance from the electrolyte layer and a second diameter at a second distance from the electrolyte layer, and further wherein the second diameter is greater than the first diameter and the second distance is greater than the first distance.
- 14. The symmetrical bi-electrode supported solid oxide 35 fuel cell of claim 11 further comprising a thin electrically conductive ceramic coating on outermost exposed surfaces of each of the first porous electrode and the second porous electrode.
- **15**. The symmetrical bi-electrode supported solid oxide 40 fuel cell of claim **14** wherein the thin electrically conductive electrical coating deposited on the outermost exposed sur-

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faces of each of the first porous electrode and the second porous electrode have essentially the same coefficient of thermal expansion as the first porous electrode, the second porous electrode and the electrolyte layer.

- **16**. The symmetrical bi-electrode supported solid oxide fuel cell of claim **11** wherein the monolith is made of substantially one material being an ionic conductor.
- 17. The symmetrical bi-electrode supported solid oxide fuel cell of claim 16 wherein the ionic conductor is selected from the group of materials consisting essentially of doped oxides of zirconium, cerium, bismuth, hafnium, thorium, indium, and uranium, and further, ionic conductors selected from the group of materials consisting essentially of yttria stabilized zirconia, partially stabilized zirconia, scandia stabilized zirconia, gadolinium doped ceria samarium doped ceria and yttrium doped ceria, and a perovskite oxide conductor, strontium and magnesium-doped lanthanum gallate.
 - 18. The symmetrical bi-electrode supported solid oxide fuel cell of claim 11 wherein the plurality of graded pores of the first porous electrode and the second porous electrode each have a small end and a large end that are oriented substantially perpendicular to the electrolyte layer, and further wherein a diameter of the plurality of graded pores at the small end is smaller in size than a diameter of the plurality of graded pores at the large end.
 - 19. The symmetrical bi-electrode supported solid oxide fuel cell of claim 18 wherein the plurality of graded pores of the first porous electrode and the second electrode are oriented such that the small ends are adjacent the electrolyte layer and the large ends are distal from the electrolyte layer.
 - 20. The symmetrical bi-electrode supported solid oxide fuel cell of claim 11 wherein the plurality of graded pores of the first porous electrode and the second porous electrode extend substantially perpendicular to the electrolyte layer, and further therein a diameter of the plurality of graded pores gradually increases in size as the first porous electrode and the second porous electrode extends away from the electrolyte layer.

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